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Abstract. We recall the basic equations of Resonant Elastic X-ray Scattering (REXS), starting from the photon-electron Hamiltonian interaction, and describing the different components for the possible transitions. We also make the connection with classical physics and we emphasize the signs of the relevant terms, resonant and non resonant, to comply to the convention on the phase wave.

1. Introduction

The variation with energy of the diffracted peak intensities around the absorption edges has been known since the 1920's, and since the first measurement of a complete spectrum, by Y. Cauchois, in 1956 [1], several works have paved the way to a good understanding of most of the important phenomena, like the studies of D. and L. Templeton on the polarization dependence [2], of V. E. Dmitrienko [3] and of K. Finkelstein[4] on forbidden reflections, of Gibbs [5], Hannon [6] and co-workers on magnetic resonant scattering, or on processes involving non simple dipole transitions again by Templeton and Templeton [7]. The current effort is on making REXS a reliable tool to extract quantitative and valuable informations from the experiments. Nowadays, data are recorded with far better resolution, polarization analysis and with many kinds of sample environments. Theory has also greatly improved even if the description of multi electronic phenomena remains a challenging task.

The purpose of the present paper is to give a brief overview of the main elements of this spectroscopy giving the key points toward the basic equations governing it. We have noticed, that some confusion takes place for example on the convention on the signs in many formulas. Different conventions are possible but very often they cannot be mixed as often done. In simple cases that does not matter, but nowadays one tries to extract tiny details from data from interference terms. Incoherent definitions or conventions become source of errors. We propose thus here not going in detail in the demonstration but insist on the units, the sign and at the end propose, modestly, a general agreement on the conventions to prefer.

Our paper is organized as follows: section 2 gives the main points to describe the interaction of polarized light with matter. From this, the formula for the resonant scattering form factor is demonstrated in section 3. The non resonant terms, Thomson and magnetic scatterings form factors are given in section 4. In section 5 we briefly recall the resonant x-ray scattering theory in the framework of classical physics. Finally, we summarize in section 6 a general convention on the notations and signs for this spectroscopy.

2. Interaction of Polarized light with matter

More general and detailed lectures exist on the interaction of polarized light with matter in text books [8] or in the context of x-ray spectroscopy [9]. Here we focus on the elastic photon in - photon out case. Related by Maxwell equations, and using the second quantization, the $\mathbf{k}$ components of the vector potential $\mathbf{A}$, the electric field $\mathbf{E}$ and the magnetic field $\mathbf{B}$ of a propagating plane wave are given by:

$$\begin{aligned}
\mathbf{A}(\mathbf{r},t) &= \mathcal{A}_0\left(ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\epsilon + a^+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\epsilon^*\right), \\
\mathbf{E}(\mathbf{r},t) &= -i\omega\mathcal{A}_0\left(ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\epsilon - a^+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\epsilon^*\right), \\
\mathbf{B}(\mathbf{r},t) &= i\mathcal{A}_0\left(ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\ \mathbf{k}\times\epsilon - a^+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\ \mathbf{k}\times\epsilon^*\right),
\end{aligned} \tag{1}$$

where a and a^+ are the annihilation and creation operators of the photon, ϵ and $\mathbf{k}$ are its polarization and wave vector and $\mathcal{A}_0$ an amplitude which is determined by imposing the energy of the photon to be $\hbar\omega$. Here we use the most common convention on the sign in the exponent of the exponential; this point is discussed later.

Relativistic effects are negligible except for the non resonant magnetic terms, they were already considered in the proceedings of the REXS 2011 conference [10]. So, here we consider only the non relativistic Hamiltonian $H = H_0 + H_I$. H_0 is the non interacting part and we focus on the interaction part between the field above and an electron of charge $-e$:

$$H_I = \frac{e}{m}\mathbf{p}\cdot\mathbf{A} + \frac{e}{m}\mathbf{S}\cdot\mathbf{B} + \frac{e^2}{2m}\mathbf{A}^2\ . \tag{2}$$

The transition operator T is given by:

$$T \approx H_I + H_I G_0(\mathcal{E}_i) H_I, \tag{3}$$

where we have used the first order approximation replacing the Green function G of the Hamiltonian H with the Green function of H_0. $\mathcal{E}_i$ is the initial state energy. G_0 is given by:

$$G_0(\mathcal{E}_i) = \lim_{\eta\to 0^+}\frac{1}{\mathcal{E}_i - H_0 + i\eta}\ . \tag{4}$$

Expanding T to the second order in e/m, one gets:

$$T = T_1 + T_{2a} + T_{2b} + \ldots \tag{5}$$

with:

$$T_1 = \frac{e}{m}(\mathbf{p}\cdot\mathbf{A} + \mathbf{S}\cdot\mathbf{B}) \tag{6}$$

$$T_{2a} = \frac{e^2}{2m}\mathbf{A}\cdot\mathbf{A} \tag{7}$$

$$T_{2b} = \left(\frac{e}{m}\right)^2(\mathbf{p}\cdot\mathbf{A} + \mathbf{S}\cdot\mathbf{B})\,G_0(\mathcal{E}_i)\,(\mathbf{p}\cdot\mathbf{A} + \mathbf{S}\cdot\mathbf{B})\ . \tag{8}$$

T_1 contains two terms linear in $\mathbf{A}$ or $\mathbf{B}$, it describes single photon processes, like absorption or emission. T_2 reveals two-photon processes, one photon in and one photon out, describing scattering processes. It is split in two terms, T_{2a}, which gives the non resonant Thomson scattering as shown in section 3, and T_{2b} responsible for the anomalous process as seen in section 4. From this, the transition probability per unit time is given by the so-called first

golden rule [8] and with the convenient normalizations, one finally gets the scattering form factor by the formula:

$$f = \frac{C_s}{-r_0} \langle \phi_f | T_2 | \phi_i \rangle \ . \tag{9}$$

The factor $C_s = -\frac{1}{4\pi\epsilon_0 c^2 \mathcal{A}_0^2}$ takes into account the photon final state density and the normalization with the incoming flux. The normalization by the classical electron radius $\frac{1}{-r_0}$ scales the result in *number of electrons*, $r_0 = e^2/4\pi\epsilon_0 mc^2$ being the elastic scattering amplitude of the free electron.

3. Non resonant form factor

3.1. Thomson scattering

We consider T_{2a} (eq. 8) inserted in equation 9. One gets the Thomson scattering form factor:

$$f_0 = \epsilon_s^* \cdot \epsilon_i \sum_g \left\langle \varphi_g \left| e^{i(\mathbf{k}_i - \mathbf{k}_s)\cdot \mathbf{r}} \right| \varphi_g \right\rangle = \epsilon_s^* \cdot \epsilon_i \int \rho(\mathbf{r}) \, e^{i(\mathbf{k}_i - \mathbf{k}_s)\cdot \mathbf{r}} d^3\mathbf{r} \ , \tag{10}$$

where $\rho(\mathbf{r}) = \sum_g |\varphi_g(\mathbf{r})|^2$ is the atomic electron density, the sum being over all the occupied states. In forward scattering one thus gets $f_0 = \epsilon_s^* \cdot \epsilon_i \ Z$, Z being the atomic number. Note that due to the minus sign in the normalisation in equation 9, the Thomson scattering *form factor*, f_0, is positive, while the Thomson scattering *amplitude*, b_0, related to the form factor by the relation $b_0 = -r_0 f_0$, is negative. In contrast to optical energies, at X-ray energies the anomalous term is small making refraction indices to be slightly less than one.

3.2. Non-resonant magnetic scattering

The non-resonant magnetic scattering was observed in 1981 by de Bergevin and Brunel [14]. The Hamiltonian was given by Blume and Gibbs in [15, 16]. It contains the interaction between the magnetic field of the incoming wave with the spin of the electron. It contains also an angular momentum part coming from the expansion to the first order in $\hbar\omega/(\mathcal{E}_n - \mathcal{E}_g)$ of the anomalous contribution T_{2b}. At high energy one gets a magnetic form factor given by $f_{mag} = -if_m$, with:

$$f_m = \frac{\hbar\omega}{mc^2} \left(\frac{1}{2} \mathbf{L}(\mathbf{Q}) \cdot \mathbf{a} + \mathbf{S}(\mathbf{Q}) \cdot \mathbf{b} \right) \ , \tag{11}$$

where $\mathbf{a}$ and $\mathbf{b}$ are two vectors depending on the incoming and outgoing wave vectors and polarizations:

$$\mathbf{a} = -2(1 - \mathbf{u}_i \cdot \mathbf{u}_s)(\epsilon_s \times \epsilon_i) + (\mathbf{u}_i - \mathbf{u}_s) \cdot (\epsilon_s \times \epsilon_i)(\mathbf{u}_i - \mathbf{u}_s) \ , \tag{12}$$

$$\mathbf{b} = \epsilon_s \times \epsilon_i - (\mathbf{u}_i \times \epsilon_i)(\mathbf{u}_i \cdot \epsilon_s) + (\mathbf{u}_s \times \epsilon_s)(\mathbf{u}_s \cdot \epsilon_i) \ - (\mathbf{u}_s \times \epsilon_s) \times (\mathbf{u}_i \times \epsilon_i) \ . \tag{13}$$

where $\mathbf{u} = \mathbf{k}/k$. $\mathbf{S}(\mathbf{Q})$ is the Fourier transform of the spin density, that is of $\rho(r)^{\uparrow} - \rho(r)^{\downarrow}$. $\mathbf{L}(\mathbf{Q})$ is related to the Fourier transform of the orbital momentum. It is often a good approximation to take $\mathbf{L}(\mathbf{Q})$ and $\mathbf{S}(\mathbf{Q})$ in the same direction. Note that the expresion of $\mathbf{a}$ is slightly different than the one in the Blume and Gibbs paper [16] (A" term in equation 2) due to a typo already reported by Fabrizi and co-workers [18].

The amplitude of the non-resonant magnetic scattering is very small and neutron diffraction is often far more sensitive to measure magnetic ordering. Nevertheless, when studying magnetic material using resonant processes, because this term interferes with the other terms, it can give notable effects on the intensity of some peaks.

4. Resonant x-ray scattering formula

Introducing the expression of the potential vector and the magnetic field given in eq. 2 in eq. 8, one can distinguish two possible processes. In the first one the emission occurs before the absorption, corresponding to a non resonant process. In the second one the absorption occurs before the emission. The former being far smaller than the latter, it will be neglected. The resonant scattering amplitude depends on transitions from an initial state $|\phi_i\rangle = |\varphi_g, (\epsilon_i, k_i)\rangle$ up to intermediate states $|\varphi_n, 0\rangle$ and from this state down to a final state $|\phi_f\rangle = |\varphi_g, (\epsilon_s, k_s)\rangle$. φ_g and φ_n represent the core and excited electron states. (ϵ_i, k_i) and (ϵ_s, k_s) are the incoming and outgoing photons with the same energy $\hbar\omega$ but different polarizations $\epsilon_{i,s}$ and wave vectors $k_{i,s}$. In this situation, where absorption is before emission, the intermediate state has no photon and we have $\mathcal{E}_i = \mathcal{E}_f = \mathcal{E}_g + \hbar\omega$ where $\mathcal{E}_g$ is the energy of the core state. The energy of the intermediate state $\mathcal{E}_n$ is the energy level of the corresponding electron with the core-hole.

Stating different core states, introducing $\sum_n |n\rangle \langle n| = 1$ on the right side of G_0 and using the fact that on the same right side in eq. 8 applies only the annihilation part of $\mathbf{A}$ and $\mathbf{B}$ and on its left side only the creation part one gets:

$$f' - if'' = -\frac{1}{m} \lim_{\eta \to 0^+} \sum_{n,g} \frac{\left\langle \varphi_g \left| \hat{O}_s^* \right| \varphi_n \right\rangle \left\langle \varphi_n \left| \hat{O}_i \right| \varphi_g \right\rangle}{\mathcal{E}_g - \mathcal{E}_n + \hbar\omega + i\eta} \tag{14}$$

where the operator $\hat{O}$ is given by :

$$\hat{O} = \left(\epsilon \cdot \mathbf{p} + i\ \mathbf{S} \cdot (\mathbf{k} \times \epsilon)\right) e^{i\mathbf{k}\cdot\mathbf{r}}\ . \tag{15}$$

At this stage we perform the Taylor expansion of the exponential up to the second order for the potential vector and to the first order for the magnetic field. Using commutator relations one gets:

$$\left\langle \varphi_n \left| \hat{O} \right| \varphi_g \right\rangle = i\frac{m}{\hbar} \left(\mathcal{E}_n - \mathcal{E}_g\right) \langle \varphi_n | \hat{o}_{E1} + \hat{o}_{E2} + \hat{o}_{M1} | \varphi_g \rangle\ , \tag{16}$$

with:

$$\hat{o}_{E1} = \epsilon \cdot \mathbf{r}\ , \tag{17}$$

$$\hat{o}_{E2} = \frac{i}{2}(\epsilon \cdot \mathbf{r})\ (\mathbf{k} \cdot \mathbf{r})\ , \tag{18}$$

$$\hat{o}_{M1} = c_m\ (\mathbf{k} \times \epsilon) \cdot (\mathbf{L} + 2\mathbf{S})\ , \tag{19}$$

where $c_m = \frac{\hbar}{2m(\mathcal{E}_n - \mathcal{E}_g)}$. Putting all this together one gets:

$$f' - if'' = m \lim_{\eta \to 0^+} \sum_{n,i} \left(\frac{\mathcal{E}_n - \mathcal{E}_g}{\hbar}\right)^2 \frac{\langle \varphi_g | \hat{o}_s^* | \varphi_n \rangle \langle \varphi_n | \hat{o}_i | \varphi_g \rangle}{\hbar\omega - (\mathcal{E}_n - \mathcal{E}_g) + i\eta}\ , \tag{20}$$

which is the basic equation in S. I. unit. Note the minus sign in front of f'' to follow the convention on its positive value. Because $\hbar\omega \approx \mathcal{E}_n - \mathcal{E}_g$ and taking into account the fact that most often the intermediate states spread into a continuum one often prefers the integral form:

$$f' - if'' \approx m\omega^2 \sum_g \int_{\mathcal{E}_F}^{\infty} \frac{\frac{1}{\pi} \sum_n \langle \varphi_g | \hat{o}_s^* | \bar{\varphi}_n \rangle \langle \bar{\varphi}_n | \hat{o}_i | \varphi_g \rangle}{\hbar\omega - (\mathcal{E} - \mathcal{E}_g) + i\frac{\Gamma}{2}} d\mathcal{E}\ , \tag{21}$$

where $\mathcal{E}_F$ is the Fermi energy and Γ is a phenomenological broadening due to the finite lifetime. $\bar{\varphi}_n$ are now electronic states normalized by the density of states. The summation on n is now only

on states at the energy $\mathcal{E}$. The equation above is monoelectronic which is a serious approximation for example at the L_{23} of $3d$ elements. To go deeper in the simulation of REXS spectra, in these cases, one has to use Multiplet formalism or a time-dependent DFT approach [13]. Bethe-Salpeter equations or even configuration techniques, supposed to be more precise, already used for XANES spectroscopy could also be used.

5. Classical X-ray Resonant Scattering

In classical physics, the photon is described by an electromagnetic field that induces an acceleration on a bound electron of charge $-e$ and mass m. The interaction is governed by the electrical force $-eE$ within Newton mechanics, the speed of electron remains sub relativistic, and we neglect the magnetic field:

$$m\ddot{x} = -eE - \eta\dot{x} - \kappa x \tag{22}$$

where $-eE$ is the force experienced by the electron in the electric field, $\eta\dot{x}$ is a damping force that tends to slow the particle, and is opposite in direction to its speed, and κx is a force that retains the particle around its average position; η and κ are both positive. For a field of the form $E_0(z,t) = E_0\ e^{i(kz-\omega t)}$, in the far field approximation [11], this equation leads to:

$$\frac{E_{rad}(r,t)}{E_0(0,t)} \quad = \quad -r_0\ \frac{\omega^2}{\omega^2 - \omega_0^2 + i\gamma\omega}\frac{e^{ikr}}{r} \tag{23}$$

where $\gamma = \eta/m$ and $\omega_0 = \sqrt{\kappa/m}$, introducing the minus sign so as to keep positive the Thomson form factor (the high ω limit), giving

$$b \quad = \quad -r_0\ \frac{\omega^2}{\omega^2 - \omega_0^2 + i\gamma\omega} = -r_0\ f\ , \tag{24}$$

with f the form factor:

$$f \quad = \quad \frac{\omega^2}{\omega^2 - \omega_0^2 + i\gamma\omega}\ . \tag{25}$$

Note that a free charge has a negative scattering amplitude which takes importance when dealing with refraction (interference with the incident field) and multiple scattering effects. When the frequency is much lower than the resonance, one finds the well-known atomic, or small particle scattering amplitude, referred to Rayleigh scattering:

$$b \quad \approx \quad r_0\frac{\omega^2}{\omega_0^2}\ . \tag{26}$$

In this case the scattering amplitude becomes positive, leading to refractive indices greater than one. One can also write expression (25) to single out a constant term and a dispersive term:

$$f \quad = \quad 1 + \frac{\omega_0^2 - i\gamma\omega}{\omega^2 - \omega_0^2 + i\gamma\omega}\ . \tag{27}$$

Close to resonances one can identify the resonant term introduced in the quantum mechanics development, if γ is small compared to ω and $\omega \approx \omega_0$:

$$f \quad \approx \quad 1 + \frac{\omega_0/2}{\omega - \omega_0 + i\gamma/2}\ . \tag{28}$$

The effect of polarization, of the direction of the electric field relatively to the scattering direction is taken into account simply by the scalar product of the incident and the outgoing electric fields, which is multiplied to the scattering amplitude.

6. Intensity and convention

6.1. Phase and diffraction vector

The phase of a propagating plane wave of energy $\hbar\omega$ and wave vector $\mathbf{k}$ is written as:

$$e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}. \tag{29}$$

This choice [12] for the phase space and time evolution imposes the signs between various quantities and requires great care in all subsequent analytical developments in resonant x-ray scattering theory. Consider the energy $\mathcal{E} = \mathcal{E}_r + i\mathcal{E}_i$ of an excited state whose decay with time goes as $e^{-t/\tau}$ with a lifetime $\tau > 0$. Convention (29) imposes $\mathcal{E}_i$ to be negative, and $\mathcal{E}_i = -\hbar/2\tau = -\Gamma/2$ with the *width* $\Gamma = \hbar/\tau$. Another example deals with the spatial phase shift taken by the photon over a small volume, like a core $1s$ orbital, leading to $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1 + i\mathbf{k}\cdot\mathbf{r}$ and giving rise to quadrupolar transitions between states of same parity. For instance, it imposes the sign on the process that consists in a dipolar absorption followed by a quadrupolar emission (so called E1E2 [6]).

The sign of the diffraction vector $\mathbf{Q}$ is also chosen, it appears when dealing with spatial phase shifts $(e^{i(\mathbf{k}_f\cdot\mathbf{r})})^* e^{i(\mathbf{k}_i\cdot\mathbf{r})} = e^{-i(\mathbf{k}_f-\mathbf{k}_i)\cdot\mathbf{r}} = e^{-i\mathbf{Q}\cdot\mathbf{r}}$, that is the choice is $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$.

6.2. Scattering amplitude and cross-section

Incident photon initially with wave function e^{ikz} are described far from the scatterer by a spherically diverging wave of the form $\frac{b(\theta)}{r}e^{ikr}$, where $b(\theta)$ is the scattering amplitude:

$$\psi \simeq e^{ikz} + \frac{b(\theta)}{r}e^{ikr}. \tag{30}$$

The probability that the photon passes through the surface $dS = r^2 d\Omega$ is $cr^{-2}|b|^2 dS = c|b|^2 d\Omega$, c being the speed of light. Normalized by the incident photon density, one obtains the scattering cross-section:

$$d\sigma_{sc.} = \quad |b|^2\, d\Omega. \tag{31}$$

The scattering amplitude induces another phase shift when photoelectric transitions toward excited states of some finite lifetime take place during the scattering process. The scattering amplitude is then a complex number. A general result in scattering theory states that the imaginary part of forward scattering amplitude is related to the total cross-section (scattering + absorption) by the so-called optical theorem [11]:

$$\sigma_{\text{tot.}} = \frac{4\pi}{k}\text{Im}\{b(0)\} \tag{32}$$

The imaginary part of the scattering amplitude should consistently be positive. The scattering form factor f, from $b = -r_0 f$, is written $f = f_0 + f' - if''$ where f_0, the free electron (Thomson) form factor which is positive, as well as the imaginary part f'' which usually is obtained from absorption measurements and taken positive to show a rising edge with increasing energy.

The total diffraction intensity is given, up to the second-order in absorption/emission photon processes, by $I(\omega) \propto |F(\omega)|^2$ where the static structure factor F is given by the expression:

$$F(\omega) = \sum_j e^{-i\mathbf{Q}\cdot\mathbf{R}_j}\left(f_{0j} - if_{mj} + f'_j(\omega) - if''_j(\omega)\right). \tag{33}$$

The sum is over all atoms j of the unit cell. Of course, when calculating intensity, the complex conjugate can be taken. This formula does not take into account the dynamical process in diffraction. A step to overcome this approximation permits to simulate the birefringence effect [10]. In this case the rotation of the polarization along the propagation of the field in the sample is taken into account. The scattering by a specific unit cell thus depends on the polarization and the amplitude of the electromagnetic field at this point in the sample.

References

[1] Cauchois Y *Comptes Rendus de l'Académie des Sciences (Paris)* 1956 **242** 100
[2] Templeton D H and Templeton L K 1982 *Acta Cryst.* A **38**, 62
[3] Dmitrienko V E 1983 *Acta Cryst.* A **39**, 29
[4] Finkelstein K D, Qun Shen and Shastri S 1992 *Phys. Rev. Lett.* **69** 1612
[5] Doon Gibbs, Harshman D R, Isaacs E D, McWhan D B, Mills D and Vettier C 1988 *Phys. Rev. Lett.* **61**, 1241
[6] Hannon J P, Trammell G T, Blume M and Doon Gibbs 1988 *Phys. Rev. Lett.* **61**, 1245
[7] Templeton D H and Templeton L K 1994 *Phys. Rev.* B **4**9 14850
[8] Cohen-Tannoudji C, Dupont-Roc J and Grynberg G 1988 in *Processus d'interaction entre électrons et atomes* chapter 2 (EDP Sciences and CNRS Editions, Les Ulis)
[9] Joly Y 2010 in *Magnetism and Synchrotron Radiation* New Trends Series: Springer Proceedings in Physics, **1**33 77 Beaurepaire, E; Bulou H, Scheurer F and Kappler J-P (Eds.)
[10] Joly Y, Matteo S D, Bunău O 2012 *Eur. Phys. J. Special Topics* **2**08 21-38
[11] Jackson, J. D., Classical Electrodynamics, 3rd ed. Wiley ed.
[12] Physicists and neutron crystallographists adopt this definition which is coherent with the time dependant Schrödinger equation $i\hbar\frac{d}{dt}\left|\psi\left(t\right)\right\rangle = H\left(t\right)\left|\psi\left(t\right)\right\rangle$. The other choice, $e^{i(\omega t-\mathbf{k}\cdot\mathbf{r})}$, is usual in the field of x-ray crystallography.
[13] Leininger P, Ilakovac I, Joly Y, Schierle E, Weschke E, Bunau O, Berger H, Pouget J P and Foury-Leylekian P 2011 *Phys. Rev. Lett.* **106**, 167203
[14] de Bergevin F and Brunel M 1981 *Acta Cryst.* A **37**, 314
[15] Blume M 1985 *J. Appl. Phys.* **5**7 3615
[16] Blume M and Doon Gibbs 1988 *Phys. Rev.* B **3**7 1779
[17] J.P. Hill and D.F. Mc Morrow 1996 *Acta Cryst.* A **52** 236-244
[18] Fabrizi F, Walker H C, Paolasini L, de Bergevin F, Boothroyd A T, Prabhakaran D and McMorrow D F 2011 *Phys. Rev. Lett.* **106** 239902